

Odd Parity and Line Nodes in Non-Symmorphic Superconductors

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Group theory arguments have been invoked to argue that odd parity order parameters cannot have line nodes in the presence of spin-orbit coupling. In this paper we show that these arguments do not hold for certain non-symmorphic superconductors. Specifically, we demonstrate that when the underlying crystal has a twofold screw axis, half of the odd parity representations vanish on the Brillouin zone face perpendicular to this axis. Many unconventional superconductors have non-symmorphic space groups, and we discuss implications for several materials, including UPt_3 , UBe_{13} , $\text{Li}_2\text{Pt}_3\text{B}$ and $\text{Na}_4\text{Ir}_3\text{O}_8$.

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Unconventional superconducting materials include heavy fermion metals [1], organics [2], and cuprates [3]. The unconventionality of these materials is reflected in the symmetry of the Cooper pair wavefunction: in contrast to their ‘conventional’ counterparts, unconventional Cooper pairing not only breaks gauge but also crystal symmetry. This opens the possibility of odd parity pairing where by fermion antisymmetry, the spins are in a triplet state.

Among unconventional superconductors, an important class are those whose order parameter vanishes somewhere on the Fermi surface. The presence or absence of these nodes determines the low energy excitations, and thus the low temperature thermodynamic and transport properties. It is generally stated that in the presence of spin-orbit interactions, an odd parity order parameter cannot have a line of nodes on the Fermi surface. This is known as Blount’s theorem [4]. In contrast, this restriction does not exist for an even parity order parameter. There are, though, several heavy fermion superconductors where Knight shift data indicate that the Cooper pair spins are in a triplet state, yet thermodynamic measurements imply the existence of a line of nodes [5].

The aim of the present paper is to investigate the generality of Blount’s arguments. Specifically, we show that in crystals with a twofold screw axis, line nodes are possible whenever the Fermi surface intersects the Brillouin zone face perpendicular to this axis, even in the presence of spin-orbit interactions. Since many unconventional superconductors have non-symmorphic space groups, it provides a large class of counterexamples to Blount’s theorem. We discuss implications for several materials of interest.

In the presence of spin-orbit coupling, spin is no longer a good quantum number. On the other hand, Anderson has shown that because of fermion antisymmetry, one can write down analogues of Cooper pair singlets and triplets [6]. By Kramers theorem, one has two degenerate states present at \mathbf{k} . Coupling them to the two degenerate states at $-\mathbf{k}$, one has an even parity state that is a ‘pseudo-spin’ singlet, and an odd parity state

that is a ‘pseudo-spin’ triplet. Blount has shown, though, that this puts restrictions on the form of the odd parity state [4]. A node requires the simultaneous fulfilling of two real equations. Since two equations in three variables are commonly satisfied on curves, and these intersect the Fermi surface at isolated points, nodes for the odd parity Cooper pair wavefunction should only occur for points on the Fermi surface. To assure that symmetry cannot force an increase in the size of the nodal regions, Blount discusses the presence of mirror planes. He argues that pseudo-spin components of the odd-parity wavefunction form an axial vector, whose components parallel and perpendicular to the plane transform according to different representations. Symmetry may only force one of these component to vanish, and therefore a larger region of zero gap is ‘vanishingly improbable’.

Blount’s symmetry considerations obviously apply to point group operations and, consequently, to any symmorphic space group. A *non*-symmorphic space group, on the other hand, contains screw axes and glide planes, i.e. the combined operation of point group elements with non-primitive translations. The latter generate additional phase factors, which in special situations may conspire in a way that *all* of the order parameter’s pseudo-spin components transform according to the *same* representation [7]. In this case, symmetry enforces the vanishing of the order parameter belonging to some representations. A particular example of such a case was encountered for the hexagonal close packed lattice of UPt_3 , where this was shown explicitly by construction from the single electron wavefunctions [8]. That is, for odd parity representations that are also odd under the symmetry operation $z \rightarrow -z$, it was claimed that all pseudo-spin components vanish on the hexagonal zone face $k_z = \pi/c$. We will employ group theory arguments to illustrate the generality of this argument.

Group Theory:—The group theory approach to Cooper pair wavefunctions of unconventional superconductors goes back to Anderson [6]. Classifications of pair states at the zone center rely on irreducible representations of point groups and have been listed for many rele-

vant crystal symmetries [9]. Building on work on anti-symmetrized Kronecker squares of induced representations [10], a more general space group approach has been developed to deduce which Cooper pair symmetries are allowed at arbitrary points in the Brillouin zone [11].

Here, we consider a general non-symmorphic space group symmetry G , containing inversion symmetry $(I, 0)$ and a twofold screw axis $(2_z, \mathbf{t}_2)$. The latter is a symmetry operation combining a π rotation 2_z around some axis with a non-primitive translation $\mathbf{t}_2 = \frac{c}{2}\mathbf{e}_z$ along the axis by half of the lattice displacement c (we choose this axis to define the z direction). $(E, 0)$ denotes the identity element and $\sigma_z = I2_z$. Also, we assume the presence of spin-orbit interactions.

The space group approach calculates representations $\mathcal{P}(\mathbf{k})$ of the Cooper pair wavefunction at a given \mathbf{k} point in the Brillouin zone by the method of induced representations [10, 11, 12],

$$\mathcal{P}(\mathbf{k}) = \sum_{\sigma} P_{\sigma}^{-} \uparrow G. \quad (1)$$

To explain this notation, we proceed in two steps: (i) we outline the construction of representations P_{σ}^{-} and (ii) we indicate a prescription how induced representations $P_{\sigma}^{-} \uparrow G$ may be calculated.

Concerning (i), representations P_{σ}^{-} at a \mathbf{k} point in the zone are constructed from small representations $\gamma_{\mathbf{k}}$ of the symmetry group of wavevector \mathbf{k} ('little group' $G^{\mathbf{k}}$). Referring for details to Refs. 10, 11, 12 we merely state the procedure: the sum σ in Eq. (1) extends over those representatives d_{σ} in a double coset decomposition $G = \sum_{\alpha} G^{\mathbf{k}} d_{\alpha} G^{\mathbf{k}}$, for which $\mathbf{g} = \mathbf{k} + d_{\alpha}\mathbf{k}$ is a vector of the reciprocal lattice. This latter condition accounts for the Cooper pair's vanishing total momentum (modulo a reciprocal lattice vector). Introducing the intersection of wavevector groups $M_{\sigma} = G^{\mathbf{k}} \cap d_{\sigma} G^{\mathbf{k}} d_{\sigma}^{-1}$, and choosing an element $a \in d_{\sigma} G^{\mathbf{k}} \cap G^{\mathbf{k}} d_{\sigma}^{-1}$, P_{σ}^{-} is then the representation of $\tilde{M}_{\sigma} = M_{\sigma} + aM_{\sigma}$ induced from $\gamma_{\mathbf{k}}$ by the following definition of its characters ($m \in M_{\sigma}$)

$$\chi(P_{\sigma}^{-}(m)) = \chi(\gamma_{\mathbf{k}}(m))\chi(\gamma_{\mathbf{k}}(d_{\sigma}^{-1}md_{\sigma})), \quad (2)$$

$$\chi(P_{\sigma}^{-}(am)) = -\chi(\gamma_{\mathbf{k}}(amam)). \quad (3)$$

Turning to (ii), induced representations are conveniently calculated with the help of the 'Frobenius reciprocity theorem' [12]. In the context of Eq. (1) the theorem states that the number of times n_j an irreducible representation Γ^j of G appears in the decomposition $\mathcal{P}(\mathbf{k}) = \sum_j n_j \Gamma^j$ equals the number of times P_{σ}^{-} appears in the decomposition of Γ^j into irreducible representations $\tilde{\Gamma}^j$ of the 'subduced' group $G \cap \tilde{M}$. Here, both Γ^j and $\tilde{\Gamma}^j$ are representations at the zone center. We summarize $\tilde{\Gamma}^j$ for points of interest in Table I. Line nodes of the odd parity Cooper pair wavefunction may arise if any of the odd parity representations $\tilde{\Gamma}_u^j$ are absent in

$\tilde{\Gamma}^j$	$(E, 0)$	$(I, 0)$	$\tilde{\Gamma}^j$	$(E, 0)$	$(2_z, \mathbf{t}_2)$	$(I, 0)$	(σ_z, \mathbf{t}_2)
Γ_g	1	1	A_g	1	1	1	1
Γ_u	1	-1	B_g	1	-1	1	-1
			A_u	1	1	-1	-1
			B_u	1	-1	-1	1

TABLE I: Characters of representations $\tilde{\Gamma}^j$ of the subduced groups. The left table applies to the group $G \cap \tilde{M}$ for a general point in the zone; the right table to the group $G \cap \tilde{M}$ for points in the planes $k_z = 0$ and $k_z = \pi/c$. Here g refers to even parity, and u odd parity representations.

the decomposition $P_{\sigma}^{-} = \sum_j m_j \tilde{\Gamma}^j$ in a symmetry plane of the zone that intersects the Fermi surface.

To apply the outlined procedure, we need to identify small representations $\gamma_{\mathbf{k}}$. Our main focus is on \mathbf{k} vectors on the zone face $k_z = \pi/c$ (ZF). For purpose of illustration we also discuss the symmetry plane $k_z = 0$ (SP) and a general \mathbf{k} point (GP). In the presence of spin-orbit interactions, spin and real space do not transform independently, and the spin rotation group is absorbed into the crystal's space group. Moreover, extra degeneracies may occur due to time-reversal symmetry. Both effects are taken into account when considering co-representations of the little group $G^{\mathbf{k}}$.

For illustration let us derive representations P_{σ}^{-} for a general \mathbf{k} point: the little group G^{GP} consists only of the identity and its multiplication with primitive translations. A co-representation γ_{GP} is characterized by the identity's character, $\chi((E, 0))$, which is two from the fact that any point in the zone is twofold degenerate (Kramers theorem). The only double coset representative satisfying the zero-momentum condition is $d_1 = (I, 0)$. M_1 is identical to G^{GP} and $a = (I, 0)$. The representation P_1^{-} is then readily deduced from Eqs. (2) and (3), see Table II. The decomposition of P_1^{-} into representations $\tilde{\Gamma}^j$ of Table I results in $P_1^{-} = \Gamma_g + 3\Gamma_u$. This corresponds to Anderson's classification of the Cooper pair wavefunction into an even parity pseudo-spin singlet and an odd parity pseudo-spin triplet. At a general \mathbf{k} point, there is no symmetry reason for any of them to vanish.

Next, we turn to points in the symmetry planes: little groups G^{SP} and G^{ZF} are both formed by $(E, 0)$, (σ_z, \mathbf{t}_2) , and their multiplication with primitive translations. To account for the appearance of non-trivial phase factors, one has to resort to the little groups' central extensions and look at their projective representations [12]. One may readily convince oneself of the absence of non-trivial phase factors for wavevectors that satisfy $k_z = 0$. For points on the zone face, however, non-trivial phase factors arise. As a result, G^{SP} and G^{ZF} define different groups. They can be identified by their multiplication table, and their co-representations can be looked up. The (relevant) characters of the co-representations are as follows: for $k_z = 0$, there are two identical co-representations γ_{SP}

characterized by $\chi((E, 0)) = 2$ and $\chi((\sigma_z, \mathbf{t}_2)) = 0$. At the zone face, on the other hand, there are two complex conjugate co-representations γ_{ZF} with characters $\chi((E, 0)) = 2$ and $\chi((\sigma_z, \mathbf{t}_2)) = \pm 2i$. The different characters $\chi((\sigma_z, \mathbf{t}_2))$ for these two cases reflect the different type of degeneracy encountered, i.e. a pairing degeneracy and a doubling degeneracy, respectively [13].

P_1^-	$(E, 0)$	$(I, 0)$	$P_{1,2}^-$	$(E, 0)$	$(2_z, \mathbf{t}_2)$	$(I, 0)$	(σ_z, \mathbf{t}_2)
GP	4	-2	SP	4	2	-2	0
			ZF	4	-2	-2	4

TABLE II: Representations P_i^- induced by $\gamma_{\mathbf{k}}$. Left table: representation for a general \mathbf{k} point. Right table: representations for $k_z = 0$ and $k_z = \pi/c$ are given by the first and second line, respectively.

Wavevectors for both symmetry planes allow for $d_1 = (I, 0)$ and $d_2 = (2_z, \mathbf{t}_2)$, resulting in $M_{1,2}$ both identical to the little group. Also, it is always possible to choose $a = (I, 0)$. Application of Eqs. (2) and (3) to $k_z = 0$ and d_1 results in the first line of the right table II [14]. Using instead d_2 leads to the identical result in the second line (thus $P_1^- \equiv P_2^-$). The decomposition into irreducible components $\tilde{\Gamma}^j$ of Table I is $P_i^- = A_g + 2A_u + B_u$, showing that half of the even parity representations (B_g) vanish for $k_z = 0$. Odd parity representations, on the other hand, are all present, indicating the absence of line nodes. This is a consequence of Blount's argument, since phase factors related to the twofold screw axis are all trivial.

At the zone face, d_1 and d_2 lead again to identical representations. Also, results for both co-representations γ_{ZF} (i.e. for characters $\chi((\sigma_z, \mathbf{t}_2)) = \pm 2i$) are identical. The result is shown in the second line of the right Table II [15]. The decomposition

$$P_{1,2}^- = A_g + 3B_u \quad (4)$$

implies that half of the odd parity representations (A_u) vanish. Eq. (4) is the main result of this paper. It shows that in crystals with a twofold screw axis, line nodes for odd parity Cooper pair wavefunctions may occur whenever the Fermi surface intersects the Brillouin zone face perpendicular to the screw axis. Our finding has relevance for a variety of unconventional superconductors.

Implications:—We first discuss the heavy fermion metal UPt_3 , which was mentioned before. Its non-symmorphic space group $P6_3/mmc$ possesses a twofold screw axis perpendicular to the $k_z = \pi/c$ face of the hexagonal zone. Two of the Fermi surface sheets intersect this zone face [16]. From our above analysis, it follows that for $k_z = \pi/c$, only those odd parity representations (of point group $6/mmm$) are allowed that are even under the operation $z \rightarrow -z$. That is, an odd parity wavefunction belonging to the representations A_{1u} , A_{2u} or E_{2u} has line nodes on the Fermi surface. This potentially clears

up a major puzzle in this material, where various measurements are consistent with a line of nodes [17], but the Knight shift indicates a spin triplet order parameter [5]. We note that an E_{2u} order parameter has been proposed to explain various experimental properties of UPt_3 [18], and recent phase sensitive measurements are in support of this proposal [19].

Another heavy fermion superconductor to which our observation applies is UBe_{13} . Again, the Knight shift suggests a spin triplet state [5], while measurements of the NMR relaxation rate find a power law consistent with the presence of a line of nodes [20]. UBe_{13} has the non-symmorphic space group $Fm\bar{3}c$ that has twofold screw axes perpendicular to the square faces of the face centered cubic zone. The Fermi surface is predicted to have pockets that intersect these faces [21]. Therefore, odd parity Cooper pair wavefunctions belonging to the representations (of point group $m\bar{3}m$) A_{1u} , A_{2u} or E_u should have line nodes on the Fermi surface.

Our next example concerns the recently discovered non-centrosymmetric superconductor $\text{Li}_2\text{Pt}_3\text{B}$ [22]. Measurements of the temperature dependent penetration depth point towards the existence of line nodes. This finding has been attributed to a mixing of even and odd parity components of the Cooper pair wavefunction [23]. In crystals without inversion symmetry, spin-orbit coupling lifts the Kramers degeneracy of the \mathbf{k} states. If the energy splitting s resulting from this is sufficiently large compared to the superconducting gap, Cooper pairs can be admixed, $\Delta_{\pm} = \psi \pm t$, with pseudo-spin singlet and triplet components, ψ and t respectively [24]. If t is large enough, Δ_- may change sign, and thus a line of nodes is possible. Given our above findings, we propose a second mechanism for the appearance of a line of nodes in $\text{Li}_2\text{Pt}_3\text{B}$ that would occur in the opposite limit of weak spin-orbit splitting of the bands. $\text{Li}_2\text{Pt}_3\text{B}$ has the space group symmetry $P4_132$. This exhibits a twofold screw axis perpendicular to the faces of the simple cubic zone. The Fermi surface of $\text{Li}_2\text{Pt}_3\text{B}$ is predicted to have several small pockets that intersect these faces [25]. If s is small enough that the mixing of odd and even parity components is not important, then Cooper pair wavefunctions belonging to the representations (of point group $m\bar{3}m$) A_{1u} , A_{2u} or E_u can have line nodes on the Fermi surface. In contrast to the first scenario, these line nodes are now constrained by symmetry. Experiments should be able to differentiate between these two scenarios.

Finally, we mention the more exotic example of $\text{Na}_4\text{Ir}_3\text{O}_8$, which is a candidate for a 3D spin liquid [26]. It has been proposed that this material possesses a 'spinon' Fermi surface [27, 28]. At the lowest temperatures, however, the specific heat decreases to zero as T^2 , indicating (within this scenario) a line of nodes on this spinon surface. This phenomenon has been recently attributed to pairing of the spinons in a mixed state as described above for $\text{Li}_2\text{Pt}_3\text{B}$ [28]. Interestingly,

$\text{Na}_4\text{Ir}_3\text{O}_8$ has the same space group $P4_132$, and the predicted spinon Fermi surface also intersects the simple cubic zone faces. Therefore, our previous discussion for $\text{Li}_2\text{Pt}_3\text{B}$ applies to this material as well, and we conclude that a pure triplet state with a line of nodes is also possible.

Conclusions:—We have shown that in some non-symmorphic superconductors, it is possible to reconcile the existence of line nodes of an odd parity Cooper pair wavefunction with the presence of (strong) spin-orbit interactions. Specifically, we have proven that Blount's theorem is superseded for superconductors possessing a twofold screw axis with a Fermi surface intersecting the zone face perpendicular to this axis. Our observation has potential relevance to a variety of unconventional superconductors and spin liquids.

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 [7] To be more specific, consider the eigenfunction of some space group element $(R, \mathbf{t})f_{\mathbf{k}} = cf_{\mathbf{k}}$ (R is a point-group operation and \mathbf{t} a translation vector). The action of time-reversal symmetry θ and inversion symmetry $(I, 0)$ generates new eigenfunctions with eigenvalues c and $e^{2i\mathbf{k}\mathbf{t}}c$, respectively, as can be checked by noting that θ and (R, \mathbf{t}) commute while $(R, \mathbf{t})(I, 0) = (E, 2\mathbf{t})(I, 0)(R, \mathbf{t})$, where E is the point group identity. It is then evident that symmetries involving non-primitive translations generate different phase factors for the different pseudo-spin triplet components at different points in the zone.
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 [14] Notice that the characters are those of double groups, and therefore for a 2π rotation, $\chi((2_z 2_z, 0)) = -1$.
 [15] Notice the additional factor -1 for \mathbf{k} points on the zone face compared to $k_z = 0$. This arises from $\chi((\gamma_{\mathbf{k}}(d_{\sigma}^{-1}(\sigma_z, \mathbf{t}_2)d_{\sigma})) = \chi(\gamma_{\mathbf{k}}(\sigma_z, -\mathbf{t}_2)) = -\chi(\gamma_{\mathbf{k}}(\sigma_z, \mathbf{t}_2))$, i.e. the action of the translation group, $e^{2i\mathbf{k}\mathbf{t}_2} = -1$. Here $d_{\sigma} = (I, 0)$ or $(2_z, \mathbf{t}_2)$ and we used the identity $(R, \mathbf{v})^{-1}(S, \mathbf{w})(R, \mathbf{v}) = (R^{-1}SR, R^{-1}S\mathbf{v} + R^{-1}\mathbf{w} - R^{-1}\mathbf{v})$.
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